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HYDRIDES AND BOROHYDRIDES OF LIGHT WEIGHT ELEMENTS AND RELATED COMPOUNDS

By

H. I. SCHLESINGER and GRANT URRY

in cooperation with
**W. HENLE, L. HOHNSTEDT, J. KERRIGAN
J. MURIB, and T. PARSONS**

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RELATED COMPOUNDS

Annual Technical Report

for the period August 1, 1953, to July 31, 1954

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August 1, 1954

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INTRODUCTION AND ABSTRACT

During the year covered by this report the major effort was placed on the newly discovered reaction between diboron tetrachloride and unsaturated and cyclic hydrocarbons. As will become apparent from the discussion of this topic in the body of this report, the new reaction seems to have considerable likelihood of becoming a valuable tool in the synthesis of organo-boron compounds and in the discovery of new types of such compounds.

Considerable progress has also been made in the study of the reaction of metallic lithium with ammoniacal solutions of pentaborane (B_5H_9). It has been shown that the metal reacts in 2 ways, in each of which 2 g. atomic weights of the metal react per mole of B_5H_9. In one reaction 2 g. atomic weights of hydrogen are generated; in the other no hydrogen is produced. The product of the first reaction has been isolated and analyzed. The second reaction is still under investigation. The possibility that this reaction will have some bearing on the interrelation of B_5H_9 and B_5H_{11} is discussed.

In this connection we have also studied the behavior of lithium toward B_5H_9 in dimethylamine. Two difficulties have caused us to discontinue this study. Lithium, at temperatures at which it does not react with dimethylamine, is only very slightly soluble in this solvent. Likewise the interaction of dimethylamine with B_5H_9 to form "amminates" is very slow at temperatures at which side reactions do not occur. During the course of these studies we have, however, obtained some information about the behavior of dimethylamine toward B_5H_9. In place of the reaction of lithium with B_5H_9 in dimethylamine we have begun an investigation of the analogous reaction in ethylamine, in which the metal is much more soluble. Preliminary results are herein reported.

The study of the reactions of hydrazine and dimethyl hydrazine with diborane and with tetramethyl diborane has been continued. Some previously doubtful aspects have been clarified. In this connection it has been found that pyrolysis of $N_2(CH_3)_2(BH_2)_2$ in the presence of diborane, or of a mixture of dimethyl hydrazine and diborane produces N-trimethyl borazole in fair yields. Unfortunately we have not yet succeeded in obtaining borazole from mixtures of hydrazine and diborane, or from hydrazine hydrochloride and lithium borohydride. We have also found that heating of the solid polymer of $N_2(CH_3)_2(BH_2)_2$ with boron trifluoride produces a volatile crystalline solid. The vapor density and the amount of hydrogen evolved suggest that the compound may be N-trimethyl, B-difluoro borazole, but the fluorine analysis has thus far been unsatisfactory.

Some though not a large amount of progress has been made on the study of borazole derivatives.

Four articles based on the work of the project have been accepted by appropriate journals for publication; 2 of these have appeared, and 2 are scheduled for publication in October 1954.

REPORT

I. The Reaction of Diboron Tetrachloride (B_2Cl_4) with Unsaturated and Cyclic Hydrocarbons

(1a) As was described in a previous report (AR 53, p.22) [1] one mole of diboron tetrachloride unites with one mole of ethylene to form a compound of the empirical composition $B_2Cl_4 \cdot C_2H_4$. Since treatment of the compound with water, as well as with sodium hydroxide solution fails to generate hydrogen even when the mixture is warmed almost to its boiling point, the boron-to-boron bond of diboron tetrachloride has evidently been severed in the preparative reaction. The structure of the compound may, therefore, be represented by the formula $Cl_2BC_2H_4BCl_2$. It has also been shown that diboron tetrachloride reacts in similar fashion with acetylene and with cyclopropane, as shown in the following paragraphs.

(b) In an exploratory experiment, 26.75 cc. of B_2Cl_4 reacted with 22.9 cc. of acetylene at $-80^\circ C$ in about 36 hours. (The abbreviation cc. is used herein to refer to the volume of material in the vapor or gaseous state at S.T.P., whereas ml. is used for the volume of liquids.) The crude product was passed into a train consisting of a -30, a -45 and a $-196^\circ C$ trap. The major portion of the reaction product was retained at $-30^\circ C$. It exhibited a vapor tension of 6 mm. at $20^\circ C$ and a vapor density corresponding to a molecular weight of about 198 (mol. wt. calc. for $Cl_2BC_2H_2BCl_2 = 189$). Its melting point lies between -130 and $-125^\circ C$. The molecular weight, although only approximate because of the small quantities used in the determination, indicates that the chief reaction product probably is $B_2Cl_4C_2H_2$. The molecular weight is far too low for a compound $(B_2Cl_4)_2C_2H_2$.

There are two possible explanations for the large melting range. Thus it is possible that the product contained a small amount of $(B_2Cl_4)_2C_2H_2$, as indicated by the observation that more than one mole of B_2Cl_4 reacted per mole of acetylene. Another possibility is that the material is a mixture of cis and trans isomers, as would be likely if the carbon-to-carbon double bond has been maintained. The matter is being studied further.

(c) Stirring of a mixture of 5.40 mmoles of B_2Cl_4 with 10.34 mmoles of cyclopropane failed to bring about reaction at $-80^\circ C$, at which temperature both acetylene and ethylene react rapidly with B_2Cl_4. At $-30^\circ C$ the reaction of cyclopropane was still very slow, but it proceeded to completion in 20 hours at $0^\circ C$. Fractionation of the product resulted in the recovery of 0.037 mmole of B_2Cl_4, and in the isolation of 0.427 mmole of BCl_3 and of a less volatile liquid.

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1. The abbreviation AR refers to Final or Annual reports. The number following the abbreviation refers to the year of those reports, e.g., AR 53 indicates the annual (final) technical report for the year ending July 1953.

Assuming that the BCl_3 had been formed by decomposition of an equal volume of B_2Cl_4, the ratio in which cyclopropane and B_2Cl_4 had combined was 1:1.01. We therefore assume the formula of the product to be $Cl_2B(CH_2)_3BCl_2$. Although the following data support this formula, further work is necessary to establish it fully.

At a pressure of 79.5 mm., .2482 g. of $Cl_2B(CH_2)_3BCl_2$ occupied a volume of 352 cc. at 98.5°C. Hence the molecular weight is 205.7 (calc. for $B_2Cl_4(CH_2)_3$ is 205.5).

Vapor tensions are as follows:

$t^\circ C$	0	12.6	26.4*	33.6	44.3	54.2	62.9*	69.1	74.0	78.9
p mm(obs)	1.0	2.4	6.0	6.7	15.4	24.4	35.9	47.1	58.0	68.0
p mm(calc)	1.3	2.8	6.1	9.0	15.4	24.4	36.0	46.8	57.3	69.7

The calculated values were obtained from the equation $\log p_{mm} = 7.8727 - \frac{2123}{T}$, according to which the boiling point would be 152°C, the heat of evaporation 9680 cal., and the Trouton constant 22.8. The data marked with an asterisk are readings taken during cooling.

Treatment of 1.12 mmoles of $Cl_2B(CH_2)_3BCl_2$ with 4.48 mmoles of methanol, led to the generation of 4.12 mmoles of hydrogen chloride (92% of that calculated on the assumption that all of the chlorine atoms are replaced by methoxy groups). Since some methanol was recovered, the reaction had apparently not gone to completion in approximately 12 hours.

(d) Further investigation of the compounds $(Cl_2B)_2C_2H_2$ and $(Cl_2B)_2(CH_2)_3$ is under way as is an attempt to prepare $(Cl_2B)_2C_2F_4$ (see sect. I(4) of this report.).

(2) Some Properties and Reactions of $Cl_2BC_2H_4BCl_2$

(a) A 0.0996 g. sample of $Cl_2BC_2H_4BCl_2$, prepared by the interaction of diboron tetrachloride (B_2Cl_4) with ethylene and carefully purified, exerted a pressure of 54.15 mm. at 123.2°C in 245.1 cc. The corresponding molecular weight is 185.7 (calc. 191.6). The melting point is -28.5 to -28.0°C. Vapor tension data are as follows:

$t^{\circ}C$	26.3	35.5	41.6	48.4	54.8	59.4	69.5	74.5	82.5	91.8
p mm(obs)	6.9	11.2	15.4	21.4	29.1	36.8	56.9	69.7	95.6	134.1
p mm(calc)	6.9	10.9	15.1	21.0	28.9	35.9	56.5	70.0	97.4	135.2

The calculated values were obtained from the equation $\log p_{mm} = 6.230 - \frac{2220}{T}$. Since the equation does not reproduce the data well at the highest temperatures, extrapolation to the boiling point was not carried out.

(b) Treatment of 1.46 mmoles of $Cl_2BC_2H_4BCl_2$ with 5.71 mmoles of methanol (a slight deficiency) generated 99.8% of the hydrogen chloride expected for complete replacement of the chlorine atoms by methoxy groups. The resulting methoxy derivative does not inflame spontaneously in air, but burns if ignited.

A 0.1003 g. sample of the compound $(CH_3O)_2BC_2H_4B(OCH_3)_2$ exerted a pressure of 58 mm. in a volume of 243.5 cc. at 108.8°C. The corresponding molecular weight is 171 (calc. 174.6). The melting point was -21.4 ± 0.6°C. Vapor tension data follow:

$t^{\circ}C$	28.3	33.2	38.2	44.1	48.9	56.7	59.2	69.2	74.5	78.5	91.6	93.3
p mm(obs)	1.4	1.8	2.6	4.0	5.3	8.2	9.7	16.5	20.2	25.8	44.3	50.1
p mm(calc)	1.4	2.0	2.8	4.1	5.2	8.1	9.3	15.9	20.9	26.0	48.2	51.4

For the calculated vapor tensions the equation $\log p_{mm} = 8.933 - \frac{2647}{T}$ was used. Although the extrapolation is more extensive than desirable, the equation leads to the values 164°C for the boiling point, 12,100 $cal/_{mole}$ for the heat of vaporization and 27.7 for the Trouton constant. Deviation from the equation probably accounts for the high Trouton constant, although association in the liquid state may be partly responsible.

(c) At a temperature slightly above -80°C, 8.97 mmoles of trimethyl amine reacted with 4.68 mmoles of $(Cl_2B)_2C_2H_4$, a ratio of 1.9:1.0. Occlusion of unchanged liquid $(Cl_2B)_2C_2H_4$ by the solid adduct apparently prevented completion of the reaction. It is ,therefore, assumed that the adduct has the composition $Cl_2BC_2H_4BCl_2 \cdot 2N(CH_3)_3$. It is a relatively stable and inert, solid, very slightly volatile material which shows little if any sign of decomposition below about 300°C. At that temperature it undergoes complex decomposition, not investigated in detail.

The adduct is insoluble, or only very slightly soluble in diethyl ether or in excess trimethylamine; it is somewhat more soluble in

benzene or tetrahydrofuran. Because of the slight volatility and solubility, molecular weight determinations have not yet been attempted. The adduct is also relatively inert chemically. Thus it does not react with hydrogen chloride at room temperature, nor does it generate hydrogen chloride when treated with methanol. With water, in which it is not appreciably soluble, it reacts only when warmed to about $40^\circ C$.

(d) Etherates of $(Cl_2B)_2C_2H_4$. Diethyl ether reacted with $(Cl_2B)_2C_2H_4$ at temperatures slightly above $-80^\circ C$, to form a white, crystalline, slightly volatile solid. Since the molar ratio $Et_2O/(B_2Cl_4 \cdot C_2H_4)$ was 1.94, the product is evidently a di-diethyl etherate. After removal of excess ether, the crystals slowly decomposed in complex fashion. The investigation of the ethyl ether reaction was undertaken primarily to ascertain whether this solvent is a favorable medium for the study of the compound, $(Cl_2B)_2C_2H_4$. Since this proved not to be the case, the matter is not being pursued further.

The tetrachloride also forms a di-dimethyl etherate. Thus 0.8 mmoles of $Cl_2BC_2H_4BCl_2$ reacted with 1.49 mmoles of dimethyl ether as the mixture was slowly warmed from $-196^\circ C$. The molar ratio of the ether to the tetrachloride was 1.88. The compound is more stable than the diethyl etherate, but decomposes slowly at room temperature. The nature of the decomposition products is now being studied.

(3) Methylation of $Cl_2BC_2H_4BCl_2$

(a) Because of the complexity of the reaction and the interest of the products formed by methylation of $Cl_2BC_2H_4BCl_2$, a special section is devoted to this topic. Description of several preparations of the tetramethyl derivative are given to illustrate the problems that have arisen in connection with a study of this reaction.

Preparation 1. The tetrachloro derivative (as the compound $Cl_2BC_2H_4BCl_2$ will be called hereafter) did not react with trimethyl boron; reaction with dimethyl zinc at about $-30^\circ C$ was violent and difficult to control. But when the latter reagent was used in the presence of trimethyl boron as a diluent, methylation proceeded satisfactorily at $-30^\circ C$.

When an amount of dimethyl zinc just sufficient to replace all of the chlorine atoms by methyl groups was used, no dimethyl zinc could be recovered from the mixture. The product formed was a homogeneous liquid as judged by the fact that it exhibits identical vapor tensions in vessels of different volumes.

At about -10° the liquid just described begins to generate trimethyl boron. The reaction seems to cease when one mole of trimethyl boron has been lost per mole of the liquid. The residue was a mixture consisting chiefly of a non-volatile, viscous material and a smaller amount of a somewhat volatile liquid, having a molecular weight (by vapor density) of about 100.

Preparation 2. The methylation was carried out in n-pentane as a solvent by use of 12.44 mmoles of dimethyl zinc and 6.20 mmoles of the tetrachloro derivative. The initial reaction occurred rapidly at $-45^\circ C$, but a period of several hours at $-23^\circ C$ was required to complete the reaction. The products were fractionated in a train consisting of -45, -63, -80 and -196° traps. The major portion of the reaction product was retained at -63°. In the $-196^\circ C$ trap 1.09 mmoles of trimethyl boron was collected. It is to be noted that this amount of trimethyl boron is relatively much smaller than the amount ultimately obtained in preparation 1.

Preparation 3. The preceding experiment was repeated with careful control of the reaction temperature, which was maintained at $-45^\circ C$ for two hours and at $-23^\circ C$ for an equal time interval. No trimethyl boron was generated during the reaction, nor during the isolation of the main reaction product. From 5.55 mmoles of the tetrachloro derivative and 11.02 mmoles of dimethyl zinc, 4.91 mmoles of product were obtained, a yield of 88.5% if the product is assumed to be $(CH_3)_2BC_2H_4B(CH_3)_2$ (hereafter to be called the tetramethyl derivative).

Of this product, 1.07 mmoles was allowed to stand for 24 hours at room temperature. During this time the amount of trimethyl boron generated was only 3% as much as that obtained from a comparable amount of the product of preparation 1 in a much shorter time at from -10 to $0^\circ C$. Even at $100^\circ C$ the sample obtained in preparation 3 was far more stable than was the product of preparation 1 at -10 to $0^\circ C$.

Preparation 4. A preparation was carried out in trimethyl boron as a solvent with conditions like those for preparation 3. The product was as stable as that obtained in n-pentane solution.

It is evident that the initial product of methylation, i.e., the tetramethyl derivative, is subject to factors which greatly affect its stability. What these factors are will become evident from the discussion of the pyrolysis of the compound.

(b) Properties of the Tetramethyl Derivative, $(CH_3)_2BC_2H_4B(CH_3)_2$. The following data support the conclusion that the initial product of methylation of the tetrachloro derivative is the compound $(CH_3)_2BC_2H_4(CH_3)_2$, and serve to characterize the compound.

Analysis was carried out by the nitric oxide catalyzed combustion with oxygen (Brown, Schlesinger and Burg, J.A.C.S. 61, 675 (1939). Results of two analyses are as follows: Wt. samples: 41.6 and 24.5 mg; B, 19.98 and 19.92, C, 65.9 and 66.1, H, 14.25% resp.; Calc. B, 19.70; C, 65.61; H, 14.69% resp.

Physical properties of $(CH_3)_2BC_2H_4B(CH_3)_2$. A 41.6 mg. stable sample of the compound in a volume of 618.1 cc. exerted a pressure of 11.5 mm. at 27.5°C, corresponding to a molecular weight of 109.7. A second determination with a 53.1 mg. sample gave a value of 110.9. Theory for $\angle(CH_3)_2B\underline{\angle}_2C_2H_4$ is 109.6. The melting points observed were -115 and -114.8°C. Vapor tension of the compound at 0° was 12 mm.

(c) The Spontaneous and the High Temperature Decomposition of $(CH_3)_2BC_2H_4B(CH_3)_2$. To learn more about the decomposition of the tetramethyl derivative, a 3.028 mmole sample prepared by method 3 was heated to 100°C in a sealed tube for 5 days. The products consisted of a volatile liquid condensable at -80°C, of non-volatile viscous material and of 3.44 mmoles of trimethyl boron.

Then the volatile liquid was warmed to room temperature in the vacuum line after removal of trimethyl boron, further decomposition occurred. Additional quantities of trimethyl boron (0.58 mmoles), of volatile liquid and of non-volatile viscous material were obtained. Thus the total amount of trimethyl boron obtained from 3.026 mmoles of the tetramethyl derivative was 4.02 mmoles. This quantity accounts for 99.75% of the total amount of methyl groups originally present in the tetramethyl derivative.

A 25.8 mg. sample of the volatile liquid when volatilized in a volume of 723 cc. exerted a pressure of 5.9 mm. at 24°C. Although the quantities involved are too small for accuracy, they indicate a molecular weight of about 112.

The experiment under discussion gave a clue to the cause of the variable stability of the tetramethyl derivative. A portion of the residue from the decomposition described above was flamed to give a white solid. To this a portion (4.14 mmoles) of carefully prepared tetramethyl derivative (which had stood for one week at room temperature without significant decomposition) was added. Decomposition set in at once with the generation of trimethyl boron. A total of 4.89 mmoles of trimethyl boron was obtained. Other products were a somewhat volatile liquid having a molecular weight of approximately 109 and non-volatile, viscous material like that obtained in preparation 1 and as a result of the 100° pyrolysis.

Evidently one (or more) of the decomposition products of the tetramethyl derivative catalyzes the decomposition. It was originally thought that preparation 1 led to an unstable tetramethyl derivative because the preparation was carried out in the same vessel in which the methylation by dimethyl zinc in the absence of solvent had been carried out--in other words that this vigorous reaction had left traces of a decomposition product in the vessel and that this product had catalyzed the decomposition. However, repetition of the vigorous, solvent-free reaction, after removal of volatile products left a non-volatile residue which did not have catalytic properties. It is further to be noted that preparation 1 seems to have produced a volatile catalyst, since the product of this preparation continued to decompose after it had been distilled away from the reaction vessel.

There are indications that inhibitors are also involved in the phenomenon. Thus, in the pyrolysis at $100^{\circ}C$, generation of trimethyl boron did not go to completion unless this product was removed from time to time. Likewise addition of n-pentane sometimes inhibited the catalytic action of decomposition residues obtained at $100^{\circ}C$, but it is possible that the n-pentane used in these cases contained traces of dimethyl zinc from previous use as a solvent, and that the zinc compound also is an inhibitor. It is our present opinion, not yet supported by evidence, that the trimethyl boron (and possibly the dimethyl zinc) acts as an inhibitor of a catalyst rather than as a product of a reversible reaction.

The phenomenon is obviously a complex one requiring further investigation.

(d) Preliminary Discussion of the Products of Decomposition of $(CH_3)_2BC_2H_4B(CH_3)_2$. Several points are to be noted in a discussion of the decomposition of the tetramethyl derivative: (1) the decomposition, irrespective of the temperature or other conditions under which it occurred, resulted in the formation of trimethyl boron, plus a small amount of a slightly volatile liquid and a much larger amount of a non-volatile glassy material which slowly lost small quantities of trimethyl boron and solidified; (2) the vapor densities of the volatile liquids, although carried out with too small amounts to be precise, indicate that the molecular weights of these liquids are either identical (between 105-112) or are very nearly the same and (3) in the spontaneous decomposition at -10 to $0^{\circ}C$ in preparation 1, 3/4 of the methyl groups of the tetramethyl derivative were recovered as trimethyl boron, whereas the pyrolysis of the tetramethyl derivative at $100^{\circ}C$ converted all of the methyl groups to trimethyl boron.

The 75% loss of methyl groups could be accounted for on the assumption that the volatile liquid has the composition $(CH_3B)_2(C_2H_4)_2$, and that the non-volatile material is a polymer consisting of

$(CH_3-B-C_2H_4-)$ units. The 100% loss of methyl groups could be accounted for on the assumption that the volatile liquid has the composition $B_2(C_2H_4)_3$, and that the non-volatile product is a polymer consisting of $-C_2H_4B(C_2H_4)_2B-$ units. The composition $(CH_3B)_2(C_2H_4)_2$ might correspond to the structure $CH_3B\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}BCH_3$, whereas the formula

$B_2(C_2H_4)_3$ could correspond to the structure $B-C_2H_4-B$. It is to be

noted that approximate vapor densities of the volatile liquids referred to are within experimental error in accordance with either the formula $(CH_3B)_2C_2H_4$ or $B_2(C_2H_4)_3$.

The preceding discussion is based not only on the observation that in the decomposition of the product of preparation 1,3/4 of the methyl groups present in the initial tetramethyl derivative had been recovered as trimethyl boron, but also on the assumption that the compositions of the volatile liquid and the non-volatile viscous material were essentially the same. It is, however, possible that even the volatile material obtained in the low temperature decomposition contained no methyl groups, and that the non-volatile material, which is always obtained in much the larger amount, still contained more methyl groups than correspond to a polymer of the type $(CH_3B-C_2H_4-)_n$.

In that case the observation that 3/4 of the methyl groups had been recovered as trimethyl boron would have been entirely accidental. Although this conclusion seems unlikely since the 75% recovery was not limited to a single experiment, it can ot be discarded without further investigation.

Unfortunately neither analysis nor molecular weight determinations can decide the question. The compositions and the molecular weights of the three substances, $(CH_3)_2BC_2H_4B(CH_3)_2$, $CH_3B(C_2H_4)_2BCH_3$ and $B(C_2H_4)_3B$, differ by amounts within likely experimental error.

Furthermore the vapor tension of the volatile liquid obtained by the decomposition of the tetramethyl derivative at -10° to 0^oC is within experimental error the same as that of the volatile liquid obtained by the 100^oC pyrolysis. (In this connection it should be mentioned that the vapor tension of the tetramethyl derivative is definitely different from that of the volatile, liquid decomposition product.) We have been attempting to decide the problem by determining whether the volatile liquid of the low temperature catalyzed decomposition contains methyl groups and, if so, how many. Thus far no reliable method has been found. The methods thus far unsuccessfully tested

are the following: (1) ^{O}xidation of the methyl groups to methanol by an ethereal solution of perbenzoic acid according to the method of Johnson and Van Campen, J.A.C.S. 60, 121(1938). The resulting esters were hydrolyzed by water; the latter was separated in part from the other and alcohol by fractionation. It was intended to determine the amount of methanol by treatment of the methanol-ether mixture with lithium hydride and measurement of the hydrogen evolved. Unfortunately we have, however, found no method of removing the last traces of water from the methanol-ether mixture without losing some of the methanol.
(2) Dichloro iodobenzene failed to chlorinate trimethyl boron which we have been using to test the efficacy of the several methods. (3) Bromination of the methyl groups to methyl bromide. Use of bromine at 150°C for 4 hours converted only about 50% of the methyl groups of trimethyl boron to methyl bromide; at 215° much hydrogen bromide was liberated. Catalytic ($FeBr_3$) and photochemical bromination gave better, but not satisfactory results. Hydrogen peroxide is now under investigation. Examination of the infra-red spectra of the compounds has had to be deferred because the infra-red spectrometer is undergoing repairs. We are also considering the use of deutero-ethylene or of the C^{14} dimethyl zinc.

(e) Other Reactions of the Tetramethyl Derivative. At room temperature, 13.24 mmoles of trimethylamine reacted with 7.01 mmoles of the tetramethyl derivative to form a slightly volatile, crystalline, white solid. Although the observed ratio of amine to tetramethyl derivative was only 1.9/1.00, the product is presumably a diamminate. It is much more reactive than the adduct $Cl_2BC_2H_4BCl_2 \cdot 2N(CH_3)_3$.

Thus treatment of the adduct of the tetramethyl derivative with hydrogen chloride regenerates 91% of the tetramethyl derivative. Some trimethyl boron and other by-products are also obtained.

(4) Attempts to Hydrogenate $Cl_2BC_2H_4BCl_2$.

Several attempts to replace the chlorine atoms of $Cl_2BC_2H_4BCl_2$ by hydrogen have been made. They have led to complex reactions, and to unstable products difficult to isolate and analyze. The tetrachloro derivative does not react with diborane in the absence of a solvent. If diethyl ether is present, one mole of the compound absorbs 1.3 moles of diborane at -80°C. During removal of the ether at -63°C, about 1 mole of diborane is lost; more is evolved at room temperature.

Reaction occurs between the tetrachloro derivative and lithium borohydride in the absence of solvent. If a considerable excess of the borohydride is used at -23°C, diborane is obtained in an amount to conform to the equation:

$$4LiBH_4 + Cl_2BC_2H_4BCl_2 \rightarrow H_2BC_2H_4BH_2 + 4LiCl + 2B_2H_6$$
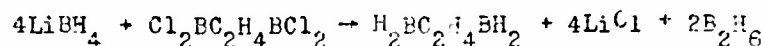
The reaction product decomposes during its removal from the solid residues by distillation. The product is more stable in ether solution. Sodium borohydride gives somewhat similar results. Although the data indicate the possibility that unstable compounds such as $(H_5B_2)_2C_2H_4$ and $(H_2B)_2C_2H_4$ may exist, especially in ether solution, the evidence as yet available does not warrant such a conclusion.

It seems possible that compounds such as $(H_2B)_2C_2H_2$ or $(H_2B)_2C_2F_4$ might be more stable than $(H_2B)_2C_2H_4$. For this reason the work on hydrogenation of the chloro derivatives is being postponed until $(Cl_2B)_2C_2F_4$ and $(Cl_2B)_2C_2H_2$ have been prepared in sufficient amount.

II. Miscellaneous Reactions of Diboron Tetrachloride.

(1) Reduction of Dimethyl Boron Bromide. In earlier reports (e.g., A.R. 49 p. 4) it was pointed out that attempts to replace the chlorine atoms of B_2Cl_4 by methyl groups by use of such reagents as dimethyl zinc leads to complete decomposition and gives no evidence of even partial formation of $B_2(CH_3)_4$. This result may mean that such compounds are incapable of existence; it may, however, merely mean that the methylating agents used are powerful enough reducing agents to reduce the boron-to-boron bonds.

We are, therefore, attempting to prepare such compounds by means which avoid the presence of strong reducing agents. One such approach is the reduction of compounds such as dimethyl boron bromide by finely divided silver. Actually we have used the trimethylamine adduct of dimethyl boron bromide, with the idea that a compound such as $B_2(CH_3)_4 \cdot 2N(CH_3)_3$ would be more stable than the simple tetramethyl diborine. For this purpose, dimethyl boron bromide (prepared by the diborane catalyzed disproportionation of trimethyl boron and boron tribromide) was distilled into a suspension of finely divided silver in a large excess of trimethylamine. The mixture was allowed to stand for a week with intermittent shaking at room temperature in a sealed tube. The tube was then opened, and the excess of trimethylamine was removed by passage through a -80°C trap. The latter retained a solid which underwent complex decomposition at room temperature. The most significant observation so far made is that treatment of the material trapped at -80° and some of its decomposition products with methanol liberated a noncondensable gas presumably hydrogen. Since none of the starting materials contain hydrogen displaceable by methanol, this observation suggests that a boron-to-boron bond has been established. The experiment is being continued.

Another reaction attempted, was the reduction of dimethyl boron bromide by lithium in liquid ammonia. Thus far the results have been

unsatisfactory, due in part to ammonolysis of the bromides. Efforts
to carry the reaction out in a way which will avoid this difficulty
are underway.

(2) Earlier study of the reaction of diboron tetrachloride with
diborane had led to unsatisfactory results (see for example A.R. 49, p 5).
We have now found that when the reaction is carried out at -23°C in
ether solution, B_2Cl_4 and B_2H_6 react in 1:1 molar proportions (e.g.
3.0 mmoles of B_2Cl_4 with 2.8 mmoles of B_2H_6). Removal of the ether
at -80° left behind a viscous straw colored liquid. At room temperature,
evaporation and condensation at -80° and -196°C separated residual
ether and diborane from a product which was retained in the -80° trap
as white crystals, but which melted at a slightly higher temperature
to a colorless liquid. Analysis of the latter gave the following data
expressed in mmoles: B, 5.72; Cl, 7.53; H (by hydrolysis with
methanol), 7.63 and Et_2O, 4.01. These results correspond within a few
per cent to the atomic (and molar) ratios $B:Cl:H:Et_2O = 3:4:4:2$.
If, however, the compound still contains a boron-to-boron bond, one
mole of hydrogen would have been produced by cleavage of that bond.
Hence the formula of the compound might well be written $B_2Cl_4 \cdot BH_3(Et_2O)_2$.
Such a formulation would agree with the observation, made in a
separate experiment, that of the original 1 mole of diborane absorbed
per mole of B_2Cl_4, one half is lost during distillation of the reaction
product. More work will, however, have to be done to permit interpretation
of the results.

III. Reactions of Hydrazine and of Dimethyl Hydrazine with Diborane and with Tetramethyl Diborane.

(1) Previous reports have described the preparation of the adducts
$N_2H_4 \cdot B_2H_6$, $N_2H_2(CH_3)_2 \cdot B_2H_6$, $N_2H_4 \cdot 2B(CH_3)_3$ and of $N_2H_4 \cdot B_2H_2(CH_3)_4$
as well as the thermal decompositions thereof, which have led to the
preparation of $N_2H_2(BH_2)_2$, $N_2(CH_3)_2(BH_2)_2$ and $N_2H_2[B(CH_3)_2]$
(See A.R. 51, p. 5; 52, pp. 8-13, 53, pp. 27-30). The compound
$N_2H_2[B(CH_3)_2]_2$ was, however, not obtained in pure condition because
we had been unable to free the starting material, $N_2H_4 \cdot B_2H_2(CH_3)_4$
from the diethyl ether which had been used in the preparation of
the latter.

(2) The Compound $N_2H_2[B(CH_3)_2]_2$ and its Dimer. The difficulty
in the purification of the compound $N_2H_4 \cdot B_2H_2(CH_3)_4$, as mentioned in
the preceding paragraph, has now been overcome by treating the crude,
diethyl ether-containing product with dimethyl ether and then removing
the latter by evaporation, a procedure which carries with it the ethyl
ether. Thus, at -80°, 4.12 mmoles of hydrazine in an excess of

diethyl ether reacted with 4.45 mmoles of tetramethyl diborane.
Evaporation of liquid left a solid which retained 68 cc. of diethyl
ether. The solid was then stirred for several hours with 567 cc. of
dimethyl ether at $-80°C$. Thereafter the liquid was removed by vacuum
evaporation first at $-80°$ and finally at $-30°C$. The ratio $N_2H_4:B_2H_2(CH_3)_4$
was 1.08 (theory 1.00), and analysis demonstrated the absence of any
but traces of impurity.

The solid product obtained by this procedure was then allowed
to warm to room temperature. Melting and evolution of hydrogen
then occurred without further heating. In an experiment in which
the hydrazine had taken up exactly 1 mole of tetramethyl diborane,
the ratio of hydrogen evolved by the solid product at room temperature
to hydrazine used was 1.91 (theory 2.0). The product of decomposition
may, therefore, be considered to have the formula $N_2H_2[B(CH_3)_2]_2$.
It is originally a liquid which fairly rapidly deposits a solid.
The latter is a dimer of the liquid as shown (1) by the fact that
its formation is unaccompanied by the production of any volatile
material and (2) by its molecular weight as recorded in the following.

A 0.1652 g. sample of the liquid, taken immediately after its
preparation and before it had deposited any solid, exerted a pressure
of 27.0 mm. when volatilized in a volume of 889 cc. at $35.5°$, corresponding
to a molecular weight of 111.6 (theory for $N_2H_2[B(CH_3)_2]_2$, 111.6).
Part of the liquid was then allowed to stand till some solid had
formed, and the vapor density of the residual liquid was then
redetermined. The data are: weight sample 0.0825 g., vapor volume
886 cc, pressure 16 mm., temperature $27.5°C$, molecular weight
109.3. Evidently formation of the solid had not altered the composition
of the liquid.

The molecular weight of the solid was determined by measuring
the lowering of the vapor tensions of solutions of it in diethyl
ether. Two determinations gave the following results: (1) wt.
sample 0.0736 g., wt. ether 1.665 g., v.t. lowering 6.65 mm., mol.
wt. 213.3. In the second determination the corresponding data
were: 0.0234 g., 0.4 g., 9.0 mm., mol. wt. 214 (The measurements
were made at $20°C$, at which the vapor tension of diethyl ether is
442.2 mm.) The solid is thus established to be a dimer of
$N_2H_2[B(CH_3)_2]_2$ (mol. wt. calc. 223).

(3) _Pyrolysis of $N_2(CH_3)_2(BH_2)_2$_. As has been reported by
Burg and Randolph (J.A.C.S. _71_, 3451 (1949)), N-dimethylamino
borine reacts with diborane or with boron trifluoride at somewhat
elevated temperatures to form N-dimethylamino diborane, $(CH_3)_2NB_2H_5$.
Similar hydrazine or dimethyl hydrazine derivatives, i.e.

$(B_2H_5)_2N_2H_2$ or $(B_2H_5)_2N_2(CH_3)_2$ might have considerable interest because of their large hydrogen content. Thus far we have, however, not succeeded in obtaining these products, although reactions of some theoretical interest have been observed. The study was begun with the compound $N_2(CH_3)_2(BH_2)_2$.

This substance was originally obtained, by pyrolysis of $N_2(CH_3)_2H_2 \cdot B_2H_6$ at about 65-70°C, as a liquid which deposited a solid polymer very slowly at room temperature and fairly rapidly at temperatures above 70°C (See A.R. 52, p. 12). In our recent repetitions of the procedure, we have had difficulty in obtaining a liquid sample which did not polymerize fairly rapidly at room temperature. The reason has not been discovered; it may possibly be that the reaction vessel employed was one which had become extensively scratched by the operation of a stirrer, and that the roughened glass surface acts as a catalyst. For this reason we have carried the experiments out with mixtures of the solid and liquid. However, a simpler procedure avoided the initial preparation of $N_2H_2(CH_3)_2 \cdot B_2H_6$ and its degradation product $N_2(CH_3)_2(BH_2)_2$ by simply heating sym. dimethyl hydrazine with diborane.

Only one of the experiments--one in which diborane and sym. dimethyl hydrazine were used--need by described, as it is typical of the results obtained in other experiments. A mixture of 6.54 mmoles of dimethyl hydrazine with 19.95 mmoles of diborane was heated in a sealed tube for 24 hours at 80-90°C after standing overnight at room temperature. After removal of the hydrogen generated (28.5 mmoles) the volatile products were passed through a train of -45, -80, and -119° traps into one at -196°C. The latter contained only diborane (7.25 mmoles). The -80°C trap contained a liquid having a 0° vapor tension of 62 mm. When warmed to room temperature it gave off hydrogen, and when purified by pumping at -80°C had a molecular weight of 61.5 and a 0°C vapor tension of 65 mm. The material generated hydrogen by hydrolysis, and probably was a mixture of B_5H_9 and B_5H_{11} (mol. wt. of B_5H_9 = 63, 0°C tension 65 mm.). The amount obtained seemed larger than would have been expected of an uncatalyzed pyrolysis of diborane, but no measurements have been made. Solids having the appearance of higher boron hydrides were also obtained.

The major volatile reaction product was retained in the -45°C trap. Two vapor density determinations made at different temperatures corresponded to molecular weights of 120.5 and 121.8 respectively (calc. for $B_3H_3(CH_3)_3H_3$, 122.4). The vapor tensions of the liquid fitted the equation: $\log p_{mm} = 7.812 - \dfrac{2009}{T}$ reported by Schlesinger, Ritter and Burg, J.A.C.S 60, 1296 (1938) for N-trimethyl borazole, as seen in the following table:

t^oC	24	29.9	34.0	38.5	48.1	53.7	58.2
p mm(obs)	10.1	14.8	17.7	22.5	36.0	46.1	56.3
p mm(calo)	11.3	15.2	17.1	23.3	36.2	46.6	56.0

The observed pressures are those of the pyrolysis product; the calculated values are those derived from the equation for N-trimethyl borazole.

Furthermore hydrolysis yielded 2.97 mmoles of hydrogen and 3.10 mmoles of boric acid per mmole of sample. Finally the presence of methylamine resulting from hydrolysis was demonstrated by treating the acid hydrolysis product with base and fractionating the volatile material in a series of traps at -45, -80 and -196^oC. The major product had a -45^oC vapor tension of 92 mm., as compared with a reported value of 94.3 mm. at -44.7 for methyl amine. There can be no doubt that the product is N-trimethyl borazole.

Extensive pyrolytic decomposition of diborane occurred. It is not certain that the reaction actually involves the diborane, but the yields of N-trimethyl borazole appear to be improved by its presence. Although the heating of dimethyl hydrazine with diborane thus appears to be a feasible method for preparing N-trimethyl borazole, other procedures involving more readily obtainable starting materials are available. A study of the most favorable conditions for the dimethyl hydrazine reaction was, therefore, not undertaken.

(4) Should the comparable reaction of hydrazine with diborane proceed in similar fashion it might be a good method for the preparation of borazole, since present preparative procedures are cumbersome. Unfortunately, however, we have thus far not obtained any volatile liquid materials from the pyrolysis of mixtures of diborane and hydrazine, or the pyrolysis of the compound $N_2H_2(BH_2)_2$ (obtained from $N_2H_4 \cdot B_2H_6$). This work thus confirms observations of Emeleus and Stone, J. Chem. Soc. (1951), 840. Similarly heating a mixture of hydrazine dihydrochloride and lithium borohydride below 80^oC produced only hydrogen, diborane and solids; at slightly higher temperature the reaction became uncontrollable.

(5) The Reaction of the Compound $N_2(CH_3)_2(BH_2)_2$ with Boron Fluoride. As already mentioned, Burg and Randolph obtained the compound $(CH_3)_2NB_2H_5$ by second method, i.e., by treatment of N-dimethylamino borine with boron fluoride. We have examined the corresponding reaction of the solid polymer of $N_2(CH_3)_2(BH_2)_2$. Thus a sample of the polymer was heated with boron fluoride in a sealed tube at 100° for 2 days. A few small drops of liquid seemed to have formed, possibly by depolymerization of $[N_2(CH_3)_2(BH_2)_2]_2$.

When the mixture was heated to 125°C for an additional 24 hours, long, transparent needles, perfect to the naked eye and quite volatile, were deposited in the cooler part of the tube. The temperature was then raised to 135° for 36 hours to make sure that as much as possible of the crystalline product had been obtained. The crystalline material was fractionated by passing its vapor several times into a -23°C trap, which retained the crystalline material and allowed the more volatile impurities to pass. The vapor tensions of the crystals were as follows:

$t°C$	24.1	24.8*	27.1	28.1	33.2	33.5	39.1	46.5	52.5	58.1	64.3
p mm(obs)	5.9	6.0	7.2	7.7	10.3	11.0	15.6	23.8	33.0	44.8	60.4
p mm(calc)	6.1	6.4	7.2	7.7	10.8	11.1	15.6	23.6	32.6	45.7	62.4

The calculated values are taken from the equation: $\log p_{mm} = 9.3978 - \frac{2564}{T}$. The value indicated by an asterisk was a measurement made after the sample had been heated to 82°C and then cooled. Except for the last two values, the data lie satisfactorily on a straight line. The vapor density of the material corresponded to a molecular weight of 142, a value which suggests that the compound may be N-trimethyl, B-difluoro borazole, $(CH_3)_3N_3B_3F_2H$. Confirmation of this formula was found by hydrolyzing a 0.0439 g. sample with sodium hydroxide solution at 110-120°C for 24 hours. The hydrogen generated thus corresponded exactly to one equivalent per mole of compound. The hydrolysate was neutralized to give a clear solution, but this formed a slight precipitate when acidified. The filtered solution was analyzed for fluorine by the method of Wichman and Dahle (J. Am. Agr. Chem., 16, 620 (1933)). The amount of fluorine formed was 0.340 mmoles, or only 1.3 moles per mole of compound instead of the 2.0 which are required by the suggested formula. It is likely that hydrolysis of the boron-fluorine bonds was not complete. Hence in spite of the agreement of the formula with the observed hydrogen content and with the observed molecular weight, the composition of the crystals remains in doubt until duplicate analyses have been made.

IV. The Reaction of Pentaborane (B_5H_9) with Lithium in the Presence of Liquid Ammonia, of Liquid Dimethylamine, and of Liquid Ethylamine.

(1) Two Types of Reaction of B_5H_9 with Lithium. Results of previous studies of the reaction of lithium with liquid ammonia solutions of pentaborane (B_5H_9) (A.R. 52, p. 23) have been erratic and difficult to interpret. For example, extraction of the reaction product with diethyl ether and subsequent evaporation of the ether from the filtered solution sometimes gave considerable quantities of a crystalline product, but at other times gave very little or none of this product. Furthermore, analyses of the crystalline material indicated that it was not homogeneous, and that it might have been impure lithium borohydride.

As the result of extended, time consuming experiments, two factors have been found which seem to be responsible for the difficulty in obtaining reproducable results. Both are related to the method of preparing the B_5H_9-liquid ammonia solutions. Thus, we have observed that when mixtures of ammonia and pentaborane are allowed to warm from $-196°$ to form the ammonia solutions, sudden pressure rise often occurs, due probably to a rise in temperature. Assuming that the heat evolution might be a cause of the difficulty, we now prepare the solutions under such conditions that the temperature at no time rises above $-63°C$. If lithium is added to a solution which has been prepared in this way and has been allowed to stand at temperatures between $-80°$ and $-63°$, 2 gram atomic weights of lithium (within experimental error) undergo reaction per mole of pentaborane used, and two equivalents of hydrogen are liberated. Furthermore, the solid residue resulting from evaporation of the ammonia from the reaction product is completely insoluble in diethyl ether, but is almost completely soluble in tetrahydrofuran.

A second point bearing on the difficulty of obtaining reproducible results is the fact that lithium may react with B_5H_9 in liquid ammonia in two ways. The first, as already described, results in the interaction of two gram atomic weights of lithium per mole of B_5H_9, and in the liberation of 2 gram equivalents of hydrogen. The second reaction involves the same amount of lithium, but produces no hydrogen. This latter reaction can be observed only if the B_5H_9 is added to a solution of an excess of lithium in liquid ammonia. We suspect that the reaction in which hydrogen is liberated is a reaction between the metal and an ammoniate of pentaborane, whereas the reaction in which no hydrogen is generated is a reaction between the metal and B_5H_9 itself. According to this interpretation, the formation of the ammoniate of pentaborane must be a reaction rapid enough to cause hydrogen evolution to occur unless the pentaborane comes into contact with lithium rapidly. Obviously reactions in which the amount of hydrogen generated is between zero and 2 equivalents can occur, depending on the rate of mixing of the lithium, ammonia and pentaborane. Actually it is almost impossible to prevent the generation of very small amounts of hydrogen.

(2) The Reaction of Lithium with B_5H_9 in Liquid Ammonia

Generating Hydrogen. The earlier work referred to in this section of the report confirmed the work of Stock to the effect that if the pentaborane and liquid ammonia are allowed to stand long enough before evaporation of the ammonia, 4 moles of the latter are retained per mole of B_5H_9. Shorter time intervals seem to result in the formation of a diammoniate. For the earlier work, we assumed that a considerable amount of time had to elapse between mixing the B_5H_9 and ammonia to assure liberations of 2 equivalents of hydrogen by the addition of lithium and that a temperature of above $-30°C$ was also needed.

We have now found that the desired result can be achieved by allowing the mixture of liquid ammonia and B_5H_9 to stand long enough at between $-80°$ and $-63°$ to cause all of the B_5H_9 to dissolve. About 3 days are usually required.

An experiment in which a week's interval at $-80°$ to $-63°C$ was allowed to elapse between the addition of lithium and the mixing of the pentaborane and ammonia involved 8 mmoles of B_5H_9, 800 mmoles of ammonia, and 16 mmoles of lithium. The amount of hydrogen liberated corresponded to a ratio: moles H_2/moles B_5H_9 = 0.93. After completion of the reaction, ammonia was removed by evaporation and several portions of diethyl ether were added to the residue, and evaporated to aid in the removal of the adsorbed ammonia. Nothing dissolved in this ether. The residue was then extracted with tetrahydrofuran. Evaporation of the filtrate left a white solid which was analyzed by methanolysis with the following results:

Molar ratio of Li:N:B:H = 5.5:6.2:13.6:32.51 = 2.02:2.28:5:11.95

These results are those to be expected for a compound $Li_2B_5H_9(NH_2)_2$, which would react with methanol according to the equation:

$$Li_2B_5H_9(NH_2)_2 + 17CH_3OH \rightarrow 2LiOCH_3 + 5B(OCH_3)_3 + 12H_2$$
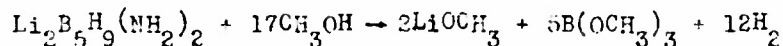
The value obtained for nitrogen in the sample just described is high, presumably because of retention of ammonia. In a second experiment, similar to the one just described, except that the ammonia and pentaborane were kept at $-80°$ to $63°C$ for a shorter time before the addition of lithium, and that ammonia was removed from the reaction product by long continued evacuation, we have obtained a product which not only gave satisfactory atomic ratios but also a satisfactory material balance. In a 141 mg. sample there were found 2.62 mmoles Li, 2.55 mmoles NH_2, 6.3 mmoles B and 15.07 mmoles hydrogen, a ratio Li:N:B:H = 2.08:2.02:5.0:11.96. Assuming that the ammonolysis proceeded according to the equation given above, only 3/4 of the hydrogen was a constituent of the original compound, since 1/4 resulted from the severance of B-B bonds. On this basis the total weight of constituents was 138.4 mg. as compared with the 141 mg. actually used.

(3) **Behavior of B_5H_9 in Dimethylamine.** Experiments have been initiated on the reaction between B_5H_9 and lithium in dimethylamine. They have, however, been discontinued for 2 reasons. In the first place, lithium is only very slightly soluble in this solvent. Only if very finely divided lithium is prepared by dissolving the metal in ammonia and then evaporating the latter, and is added to dimethylamine, is a blue

color noted. If pieces of lithium are used, the rate of solution is apparently slower than the rate of reaction with dimethylamine, because no color is observed. The second difficulty is that if mixtures of dimethylamine and B_5H_9 are allowed to stand at temperatures between -80° and $-45^\circ C$ for 3 to 4 days and the excess of amine is then distilled away, 4.33 moles of the latter are retained per mole of B_5H_9. It therefore seems likely that under these conditions some cleavage of B_5H_9 occurs. If, on the other hand, the temperature is maintained at $-80^\circ C$, not all of the B_5H_9 reacts with the amine.

Because of these difficulties we have discontinued the study of this reaction. We have, however, incidentally made some observations about the behavior of liquid dimethylamine toward B_5H_9. Thus, a mixture containing 3.92 mmoles of B_5H_9 and 60.3 mmoles of $(CH_3)_2NH$ was stored at temperatures between -80 and $-45^\circ C$ for 14 days. The excess amine was then distilled away at $-80^\circ C$. The amount of amine retained after 24 hours of pumping without further loss (namely 23.8 mmoles) corresponded to a ratio $(CH_3)_2NH/B_5H_9 = 6.07$.

The residue, $B_5H_9 \cdot 6N(CH_3)_2H$ was a glassy material. When it was warmed to $0^\circ C$ it melted and more dimethyl amine was lost. After a few minutes a white solid of crystalline appearance was formed. The total amount of dimethyl amine recovered now amounted to 48.5 mmoles, leaving 11.8 mmoles combined with the 3.92 mmoles of B_5H_9 originally used, a ratio $(CH_3)_2NH/B_5H_9 = 3.00$.

The material just described melts at about 60° forming a partially volatile liquid. Removal of the volatile portion leaves a crystalline deposit. This latter part of the reaction has not been investigated.

(4) _The Reaction of Lithium on Pentaborane in the Presence of Ethylamine._ Unless the ethylamine is purified, addition of lithium causes separation of the liquid into two layers, one of which seems to be a solution of lithium in ammonia. By pumping for about 2 days on 100 g. of Eastman ethylamine maintained at $-80^\circ C$ the ammonia is removed, but some amine is lost. In an experiment with the purified material, a mixture of about 5 ml. of ethylamine with 2.82 mmoles of B_5H_9 was allowed to stand for 3 days. To the solution 6 mmoles of lithium wire was added. The reaction appeared to be complete in about 5 hours at $-63^\circ C$--a reaction which is slower than the analogous reaction in liquid ammonia. In the reaction 4.34 g. equivalents of hydrogen was liberated, a ratio $H/B_5H_9 = 1.5$ instead of the expected

2.0. From the reaction product the excess ethylamine was allowed to pass into a $-196^\circ C$ trap through one at $-63^\circ C$. In the latter a liquid of much lower volatility than that of ethylamine collected. When the solid residue in the reaction vessel was heated slowly to

80°C additional hydrogen (0.6 mmoles) and ethylamine were liberated. These results are as yet difficult to interpret, possibly because the initial reaction with lithium actually was not complete. The investigation is being continued by using a larger amount of the metal and possibly a higher temperature. (Lithium reacts so slowly with ethylamine that in 4 days at -80° to -63°C only about 1/2 cc. of hydrogen was liberated by 8 mmoles of lithium.)

(5) The Reaction of Lithium on B_5H_9 Without Generation of Hydrogen in the Presence of Liquid Ammonia. In 3 different experiments we have been able to carry out the reaction between lithium and B_5H_9 in liquid ammonia under such conditions that not more than 0.07 mmoles of hydrogen were liberated per mmole of B_5H_9 at -80°C. To achieve the same result with larger quantities, vigorous stirring is necessary. Furthermore 90% of the excess ammonia can be removed without loss of hydrogen. To rid the residue of the last 10% of ammonia, dimethyl ether was added and evaporated. The residue was then extracted with a mixture of dimethyl ether and tetrahydrofuran. Unfortunately during filtration of the mixture, hydrogen was generated at the sintered disc which had not been cooled. Further work is in progress.

The interest in this reaction lies in the possibility that a lithium adduct of B_5H_9 might prove to be a derivative of B_5H_{11}.

V. Derivatives of Borazole

Little progress has been made in this aspect of our investigation. We have prepared a sample of B-dichloro, B-monomethyl borazole by treatment of trichloroborazole with dimethyl zinc in toluene as a solvent. The reaction was allowed to proceed for 17 hours at about 85°C. Analysis of the product after purification by fractionation gave the following values: found, Cl 41.3, B 18.9% (calc. for $Cl_2(CH_3)B_3N_3H_3$, Cl 43.4, B 19.8%). The ratio of B/Cl found was 1.5 in full agreement with the calculated value. The data indicate slight contamination with the solvent.

Efforts to prepare B-monochloro, B-dimethyl borazole have not been successful so far. The products obtained have been mixtures which appear to undergo disproportionation during separation.

VI. Publications

Preparation of Borazole by the Reduction of Trichloroborazole. By R. Schaeffer, M. Steindler, L. Hohnstedt, H. Smith, L. Eddy and H. I. Schlesinger, J.A.C.S., 76, 3303 (1954).

Preparation and Some of the Properties of Diboron Tetrachloride (B_2Cl_4). By G. Urry, T. Wartik, R. Moore, and H. I. Schlesinger. (Scheduled for publication in October.)

Diboron Tetrachloride, B_2Cl_4, as a Reagent for the Synthesis of Organo-Boron Compounds I. The Reaction of Diboron Tetrachloride with Ethylene. By G. Urry, J. Kerrigan, T. Parsons and H. I. Schlesinger. (Scheduled for publication in October.)

A Simple Electrical Control for Automatic Toepler Pumps. By L. Hohnstedt and M. Steindler. Review of Scientific Instruments, 25, 296 (1954).

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